Leuven lab discovers selective recycling process

As the name implies, rare earths are not as abundant as some commonly-used elements. And yet many of them are vital components in a range of modern technologies; hence the constant debate in recent years surrounding supply threats. Recycling is therefore an important consideration where rare earths are concerned, and this article examines a more sustainable and energy-efficient alternative for the recycling of lamp phosphor waste. To date, the process only applies to laboratory conditions.

Figure 2: Urban mining efforts such as the recycling of fluorescent lamps can help guarantee a sustainable supply of critical elements.

The rare earths are a group of metals that are essential to modern-day technologies such as hard disk drives, wind turbines, electric cars, energy-saving light bulbs and speakers. The two main markets for rare earths are strong permanent magnets and fluorescent lamp phosphors, together accounting for 70% of the value of the rare-earth market. Other applications such as polishing powders attract very large volumes of rare earths but have a lower added value.

Today, over 90% of the world's production of rare earths is situated in China, thus raising fears of market distortion and supply constraints. The price of these metals continues to be highly volatile even though worldwide efforts are being undertaken to restart old mines and explore new deposits outside of China. While primary mining is certainly important, it has two major drawbacks:

• The environmental burden and disposal of radioactive elements (thorium) associated with the processing of the rare-earth-containing ores. The processing and purification of these ores requires large amounts of acids and organic solvents.

• The large mismatch between supply and demand for the different rare earths. This phenomenon, called the 'balance problem', is very pronounced for rare earths owing to the fact that these elements are always present as a group in the ores but only some of them have a sizeable market. These critical rare earths are neodymium and dysprosium for strong permanent magnets and europium, terbium and yttrium for the lamp phosphors used in fluorescent lamps. Enough ore has to be mined every year to satisfy the demand for these five elements, creating very large overproduction of other, more common rare earths such as lanthanum and cerium. A large amount of energy also goes into the difficult separation of the individual rare earths.

Collection and recycling technology

This is where recycling comes in. Recycling of end-of-life consumer products could help in closing the loop for these critical rare earths by recovering them in the same ratio that is needed for the manufacturing of new products. Recycling could also help shift the production of rare earths to Europe and the USA given that most consumer products containing rare earths are made for these markets. Two aspects of recycling must be addressed: collection and also recycling technology. For most products, collection is the biggest bottleneck. The reuse of industrial manufacturing scrap is therefore one of the first matters to be considered but about which very little is known because company production secrets may be involved.

Recycling from end-of-life consumer products requires a more elaborate collection effort. Some car and air-conditioning manufacturers are considering the recovery of valuable neodymium-iron-boron magnets from their end-of-life products, but the best collection rate at present is observed for fluorescent lamps. In most Western countries, collection of these lamps is mandatory and organised by the government owing to the presence of trace amounts of mercury. Most of the time, however, the lamps are simply dismantled to safely dispose of the mercury and sometimes also recycle the glass, but nothing is done with the rare-earth-containing phosphor powders.

Critical and less critical

These phosphor powders convert the ultraviolet light generated by the mercury in the lamp into green, red and blue visible light, which together are perceived as white light by the human eye. These phosphors contain significant amounts of the critical rare earths yttrium, terbium and europium, as well as the less critical lanthanum and cerium. Unfortunately, the lamp phosphor waste also contains large amounts of less valuable products such as the broadband white halophosphate phosphor 'HALO', alumina and glass particles.

An overview of the phosphor powder composition is given in the table accompanying this feature. The most valuable component by far is the red phosphor YOX, which holds 80% of the rare earths and 70% of the value in the lamp phosphor powder.

Waste and energy challenges

In 2012, Solvay launched a recycling operation at La Rochelle in France for the annual treatment of around 2000 tons of phosphor waste. The company's patented process is based on the total dissolution of the lamp phosphor waste using a variety of acidic, alkaline and high-temperature attacks. All the elements are then separated by multiple-stage solvent extraction to produce pure rare earths. This process is very effective but is relative long and therefore requires significant amounts of chemicals and energy. Researchers worldwide are therefore looking at innovative ways to process this waste more efficiently. There are two main technical challenges associated with the treatment of lamp phosphor waste. The first is the unwanted dissolution of the non-valuable HALO: this phosphor is very easily dissolved in diluted acidic solutions, and since it can make up almost 50% by weight of the waste, it leads to substantial acid consumption and pollutes the solution with unwanted elements, which in turn generates waste.

The second challenge concerns the processing of the very inert phosphors LAP, BAM and CAT. These are currently subjected to a high-temperature process called alkaline fusion: a source of oxygen such as Na_2O, NaOH or Na_2CO_3 is mixed with the phosphor powder and then heated at 700–1000 °C to convert all the elements into oxides, which can then be dissolved in nitric acid. This process is quite energy-intensive and researchers are therefore also looking at ways of significantly reducing the required temperature.

Achieving selectivity

Recently, we published a front-cover article in the 'Green Chemistry' journal* outlining a new, patented recycling process that addresses the unwanted dissolution of HALO. In this process, the most valuable component in the lamp phosphor powders, namely YOX, is dissolved selectively and the phosphor can be regenerated at the end of this three-step process.

To achieve this selectivity, we used an acid-functionalised ionic liquid called betainium bistriflimide. Ionic liquids are organic solvents which consist entirely of ions and which are liquid below 100 °C. The fact that they consist entirely of ions gives them some unique properties such as negligible vapour pressure (no evaporation), low flammability and relatively low toxicity, especially compared to other organic solvents. Ionic liquids are also often considered designer solvents owing to the endless different combinations of anions and cations to form ionic liquids.

A specialised, task-specific ionic liquid can therefore be designed for each particular application in order to meet its requirements in the best possible manner. The ionic liquid used in our process contains betaine as cation and a bistriflimide anion: betaine is used worldwide as a food additive for animals and bistriflimide anions are used as electrolyte in lithium-ion batteries. The wide availability of both components and the convenient one-step synthesis of this ionic liquid render it relatively affordable to make, despite

OVERVIEW OF THE APPROXIMATE LAMP PHOSPHOR WASTE COMPOSITION

Name	Formula	Waste fraction [a] (wt%)	Value
HALO	$(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2 : Sb^{3+}, Mn^{2+}$	50	Low
YOX	$Y_2O_3 : Eu^{3+}$ (red)	20	High
BAM	$BaMgAl_{10}O_{17} : Eu^{2+}$ (blue)	5	Low
LAP	$LaPO_4 : Ce^{3+},Tb^{3+}$ (green)	5	High
CAT	$CeMgAl_{11}O_{19} : Tb^{3+}$ (green)	5	High

[a] Approximate fraction found in lamp phosphor waste; the remaining consists of SiO_2 and Al_2O_3.
* The full paper can be consulted for free: D. Dupont, K. Binnemans, Green Chemistry, 2015, 17, 856-868

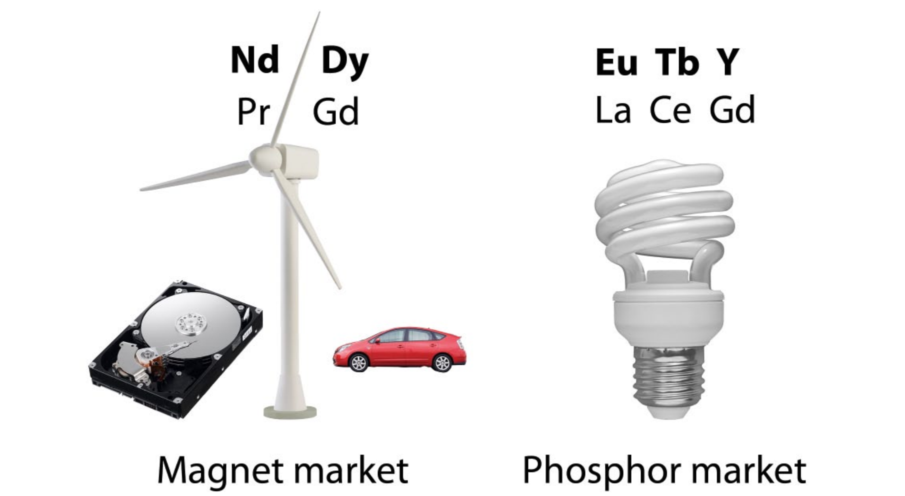

Figure 1: The main markets (by value) for rare-earth elements are the NdFeB magnets used in electronics, hybrid cars and wind turbines and the lamp phosphors used in fluorescent lamp tubes and compact fluorescent lamps.

its seemingly complex structure. The acidic group on the betaine cation (indicated in red on the figure) makes this ionic liquid very suitable for the dissolution of metal oxides. In particular, we saw that we could dissolve the red phosphor YOX without dissolving the other components. This cannot be achieved in water with traditional acids because the non-valuable HALO will always go in solution prior to the YOX. As mentioned, this consumes large amounts of acids and pollutes the water with unwanted elements, which then requires many additional process steps to recover the pure rare earths.

The reason behind this selectivity would lead us too far for this feature, but it suffices to say that the ionic liquid has a particular affinity for the dissolution of metal oxides. Other commonly-known water-soluble compounds such as table salt do not dissolve in this ionic liquid. The selective dissolution of the red phosphor YOX also means that no purification (solvent extraction) steps are necessary. The dissolved yttrium and europium can be removed from the ionic liquid by precipitating with solid oxalic acid – a common process in the rare-earth industry because it is very efficient and selective. The mixed yttrium/europium oxalate is a solid, which is used as precursor for the synthesis of new YOX phosphor. By calcining this material in an oven, the oxalate is transformed into YOX and CO_2.

Fully regenerated

On testing the resulting red phosphor, it was found to have approximately the same quality and luminescence as the commercially-available product. By optimising the calcination step, a high quality YOX could be prepared which would meet industry standards. It is also important to stress that the ionic liquid is fully regenerated during the precipitation step and that it can therefore be reused as such. The reusability of the ionic liquid is important considering that it is a relatively expensive solvent. This process thus recovers 70 % of the value in the phosphor waste by selectively recovering the most valuable component, YOX. The remaining value is held in the green phosphors, which require much harsher conditions (700–1000 °C) to be processed. However, the terbium content in this residue justifies further attempts to try and find a method to process these phosphors at lower temperatures. We are currently working on different ideas to recover these phosphors too, at temperatures below 200 °C. A schematic overview of the recycling process for YOX is given in this feature:

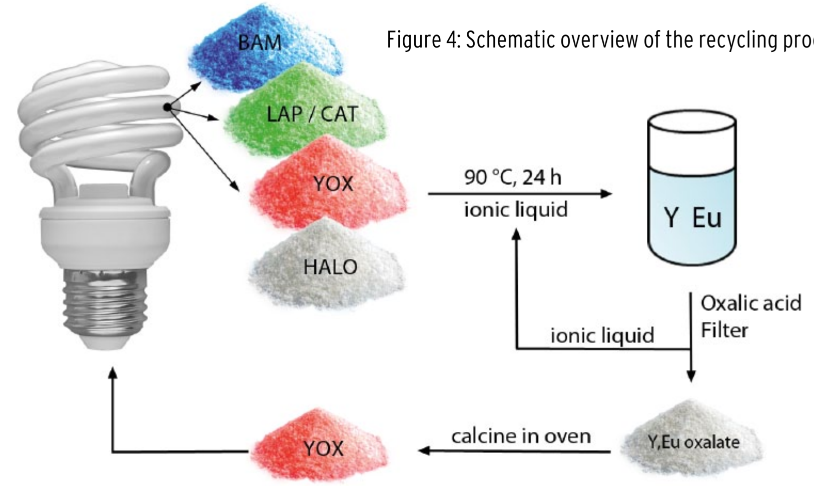

Figure 4: Schematic overview of the recycling process.

The process consists of three main steps:

1. The phosphor waste powder is stirred in the ionic liquid for 24 hours at 90 °C to selectively dissolve the red phosphor YOX.
2. The yttrium and europium dissolved in the ionic liquid are removed with solid oxalic acid. Oxalic acid precipitates the yttrium and europium as a mixed oxalate and regenerates the ionic liquid.
3. The oxalate precipitate can be calcined in an oven at high temperature to obtain the pure red phosphor, which can be used again for the manufacturing of new fluorescent lamps.

Economic advantage

The main economic advantage of this process is that it avoids the use of complex solvent extraction plants, which require very large investment. The separation of individual rare earths with solvent extraction requires hundreds of consecutive counter-current mixer settlers to obtain sufficient purity. By avoiding the contamination in the first place through our selective leaching procedure, we eliminated entirely the need for solvent extraction. The apparent simplicity of this process should allow it to be built on-site close to recyclers.

A second important advantage is that no wastewater is generated because the dissolution of HALO is avoided. The dissolved YOX is reused in the end to make new YOX in a process that only produces CO_2 and no side products.

Using a selective dissolution of the most valuable component in lamp phosphor waste powder, we can recover 70 % of the value without generating any extra waste. The ionic liquid, required for this process, is also entirely reusable. Therefore, we hope the resulting recycling process offers a more sustainable and energy-efficient alternative for the recycling of lamp phosphor waste.

The patent for this process is currently held by the KU Leuven university in Belgium, but we are working in close collaboration with interested industrial partners with a view to perhaps bringing this technology to the market. Our different research consortia such as RARE3 (www.rare3.eu) are aiming to bridge the gap between academia and industry in an attempt to find breakthrough solutions for rare-earth recycling and technology.

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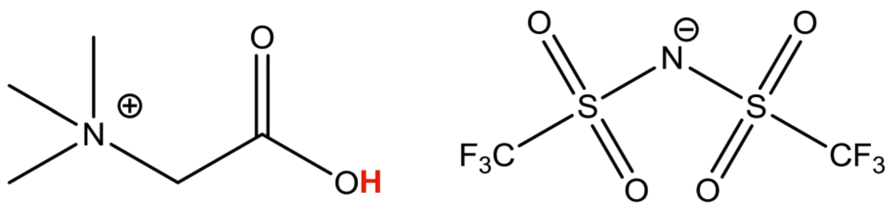

Figure 3: Chemical structure of the ionic liquid "betainium bistriflimide".

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